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CALCIUM CARBIDE AS A METALLURGICAL REDUCING AGENT

BY

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CALCIUM CARBIDE AS A METALLURGICAL REDUCING AGENT

INTRODUCTION

The disulphurization of sulphide ores or pig iron by a simple process of oxidation is very far from complete. But if disulphurization is to be thorough, it must be, by converting the sulphur into calcium sulphide, which is universally carried out at present by adding lime to the molten mass of impure metal; the reaction takes place in the following manner:

$$FeS + CaO + C = CO + Fe + CaS.$$

The CaS is then removed by the slag.

In this work, the object is to remove the sulphur as CaS, but it differs from the ordinary method, in that CaC_2 is employed in place of CaO. This is to be carried out by heating iron sulphide with the carbide at some definite high temperature, the iron sulphide acting as a representative sulphide ore. In narrowing down the purpose of this work to the most concise wording, it is to study the reactions of calcium carbide with ferrous sulphide, and determine whether these reactions can be applied in desulphurizing steel.

HISTORICAL.

From the earliest date in the history of metallurgy it has been recognized that sulphur and phosphorus are harmful elements in steel, and the problem of their elimination has not been thoroughly solved. Among the many methods and reagents that have been employed, comparatively little has been done with calcium carbide.

It seems advisable to state the manufacture, properties, and reactions of calcium carbide now, so that the reader will understand why certain methods of attack have been used later on.

Calcium carbide was first prepared by Woehler in 1862, by heating an alloy of zinc and calcium to a welding temperature.[1] It was not until Wilson's discovery in 1892 that it could be commercially manufactured in the electric furnace. This process consists of heating a mixture of finely pulverized limestone and coke, in an electric arc at a temperature of 1600 degrees centigrade. The reaction which takes place in the furnace is as follows:

$$CaO + 3C = CaC_2 + CO \text{ -- } 105350 \text{ calories.}$$

Theoretically, this reaction would require a mixture of 875 parts by weight of lime to 563 parts of carbon, but in actual practice about 650 parts of carbon are needed, since some of it is consumed in other ways than by the above reaction.

The carbide as taken from the electric furnace is hard and crystalline, but loses its luster on exposure to air, especially when moist, and finally crumbles to a gray powder, containing many graphite particles. It may be kept unchanged in a well closed bottle; best in the presence of coal-oil. When pure, it is colorless, but small amounts of foreign matter render it reddish brown or black.[2]

The specific gravity is 2.3 and the melting point is in the neighborhood of 1800 degrees centigrade.[3] It is easily decomposed by water to form calcium oxide and acetylene, the chemical equation being as follows:

$$CaC_2 + H_2O = C_2H_2 + CaO.$$

Theoretically, one pound of carbide should require .525 pounds of water for its decomposition and the products formed should be 1.156 pounds of lime and .4064 pounds or 5.585 cubic feet of acetylene at zero degrees centigrade. But on account of the impurities, the best results obtained have been 5 Cu. Ft. of acetylene. Upon decomposition of one pound of the carbide, 900 B.T.U. are liberated.[4]

If the carbide is heated in hydrogen, a little tarry matter and a slight white sublimate are formed, but it is otherwise unaltered, even after long heating. Heated in air, the same tarry substance is formed, but no other action is apparent; even with oxygen, the carbide is unaffected until a very high temperature is attained, when the materials glow brightly, yielding a white powder.

Hydrochloric acid has no action in the cold, but on heating, it causes the carbide to swell up and become dirty gray. A small quantity of colorless liquid distills over, white fumes are evolved, and a part of the solid fuses, being converted into calcium chloride.

Chlorine is also without action in the cold; at a temperature of 245 degrees C. it causes the carbide to glow brightly, to swell and to fuse together, while a slight yellowish-white sublimate is formed; the fused mass is calcium carbide. Bromine reacts at 350 degrees C., and sulphur vapors at 500 degrees C. The products of the last reaction are calcium sulphide and carbon disulphide. Petroleum, benzine, carbon disulphide and carbon dioxide do not have any effect.

Strong sulphuric acid in the cold gives a few bubbles with calcium carbide, but on heating, the action is increased and continues after the source of heat has been removed. Strong nitric acid produces red fumes, but the gases from this and from the sulphuric acid, burn with a luminous flame. A solution of sulphuric acid and potassium bichromate react violently with the carbide, forming a non-inflammable gas. The carbide acts as a reducing agent to many oxides, and if present in excess, tends to allow the calcium to combine with the reduced metal. In this manner, alloys with iron and other metals are formed. Iron containing calcium, approaches in appearance, that of ferro manganese, being more brittle and easily oxidisable in contact with water.[5]

If an excess of litharge be heated to redness in contact with the carbide in a clay crucible, the reaction is accompanied by vivid incandescence, resulting in the formation of metallic lead and calcium oxide; but with certain calculated proportions of the litharge and carbide, an alloy of lead and calcium is formed which is more or less brittle, having a melting point lower than pure lead.

Stannic oxide, cupric oxide, and ferric oxide at high temperatures are readily reduced, giving results of no practical value. In a further operation, oxides of manganese, nickel, cobalt, chromium, molybdenum, and tungsten were readily reduced, yielding calcium alloys.[6]

Since calcium carbide is a deoxidizing agent, it will therefore, when added to a metal in the state of fusion which is always slightly oxidized, react in the following manner:

$$(1)\ CaC_2 + 2MO = 2CO + Ca + 2M.$$

It is evident that under these conditions, as one part of the carbide only takes part in the above reaction, the utilization of this compound is not to the best advantage. To increase its power, a

metallic chloride, RCl, which must be dehydrated,[7] may be added; the Cl will combine with the Ca set at liberty, in such a manner, that the two affinities of the C for the O, and of the Ca for the Cl, will act simultaneously, giving the following reaction:

(2) $CaC_2 + 2RCl + 2MO = 2R + 2M + CaCl_2 + 2CO_2$.

These reactions may be applied either to the extraction of a metal from its ores, or for the manufacture of metallic alloys, according to whether the metallic chloride used corresponds with the metal or not. If M=R, we obtain the metal only; if not, we obtain the alloy R + 2M. As an example of this formula we can give the preparation of aluminum bronze, which consists of gently heating a mixture of alumina and chloride of copper, in contact with calcium carbide.

In an article taken from the Journal of Society of Chemical Industry (1902, page 1302) the above reactions (1) and (2) are stated to react in the following proportions by Neuman:

(3) $CaC_2 + 3M_2O = 3M_2 + CaO + 2CO$.

(4) $2MCl + 2M_2 + CaC_2 = 3M_2 + CaCl_2 + 2CO$.

But Kugelgen said that the above reactions take place as follows:

$CaC_2 + 5M_2O = CO_2 + CaO + 5M_2$ and

$2MCl + 4M_2O + CaC_2 = 5M_2 + CaCl_2 + 2CO_2$.

Alumina which cannot be reduced by carbon even at a white heat, is reduced by the carbide in the following manner:

$Al_2O_3 + CaC_2 = 2Al + 2CO + CaO$.

Calcium carbide is also a reducing agent for many sulphides. Pyrites, tetrahedrites, galena, stibnite, and magnesium sulphide are all reduced when heated with the carbide in an electric furnace, leaving calcium sulphide; but all the metals, except the iron of the pyrites, and the copper of tetrahedrite are volatilized. Aluminum sulphide is not reduced when thus treated.[8]

It may seem from the first paragraph of this article that phosphorus and sulphur have no beneficial effects when present in iron or steel, but to be sure, they have their virtues as they have faults, of course, the latter being considerably more numerous than the former. Phosphorus is probably the most injurious impurity found in steel with the possible exception of the occuluded gases such as oxygen, hydrogen, and nitrogen. The ill effects of phosphorus are very apparent when the steel is cold. It produces the phenomena of "cold shortness" or brittleness when cold, either in hardened or annealed steels.[9] This brittleness is especially noticeable when the steels are subjected to vibratory stresses or to shock. The ductility is very little affected when the loads are slowly applied. Experiments have proven, that in amounts up to .12 per cent, phosphorus increases the strength under slowly applied loads. Under shock however, this material was a failure. The bad effects of phosphorus increase as the carbon content is increased, due to the formation of coarse crystals which tend to produce brittleness.

Phosphorus produces a phosphide of iron, Fe_3P, which forms a series of alloys with iron. The eutectic of this series contains 69 per cent of the phosphide or 10.24 per cent of phosphorus, and is very brittle. A small amount of phosphorus will dissolve in the iron, forming no brittle eutectic, but as the carbon is increased, it precipitates the phosphorus from the solid solution into the brittle eutectic form. Thus the lower the carbon, the more phosphorus may be present without being seriously injurious.

Phosphorus increases the tensile strength of steel somewhat as does carbon, but does not decrease the ductility as rapidly as does carbon. Phosphoretic steels resist wear better than steels with a lower phosphorus, and high phosphorus is permissable or even desir-

able if the steel is to resist abrasion only, and no shock or vibration is to be encountered. Phosphorus increases the hardness of steel without lowering the electric conductivity as much as other hardening elements. For this reason, high phosphorus steels are used for third rails of trolley systems.

High phosphorus steels are used for screw machine products, where shock strength is not a requisite, as it gives excellent machining properties, producing clean bright surfaces, and increasing the tensile strength.

Sulphur occurs in commercial steels as manganese sulphide, and when manganese is absent the sulphur is present as FeS, of which the former sulphide is a less harmful constituent; the reason being that FeS spreads out in webs or sheets instead of coalescing in drops as MnS does. Steels for several purposes such as that used for longitudinal strength are benefited by a certain amount of manganese sulphide; sulphur in low carbon steels improves the free cutting properties. Sulphur is considered most harmful at rolling temperatures, since during this process the steel is liable to crack. Steel employed in places where it is exposed to corrosion, must have all the sulphur removed, since sulphur promotes corrosion rapidly.

In the present day manufacture of steel in the United States sulphur and phosphorus are removed by the Basic Open Hearth process, while in England and Germany, these elements are eliminated by the Basic Bessemer process, the difference in choice of the two processes being attributed to the contents of the raw materials found in the above three countries.

In the Open Hearth process,[10] the sulphur and phosphorus, also silica with several other impurities, are removed by the slag. Steel scrap is spread over the bottom of the furnace; this is covered

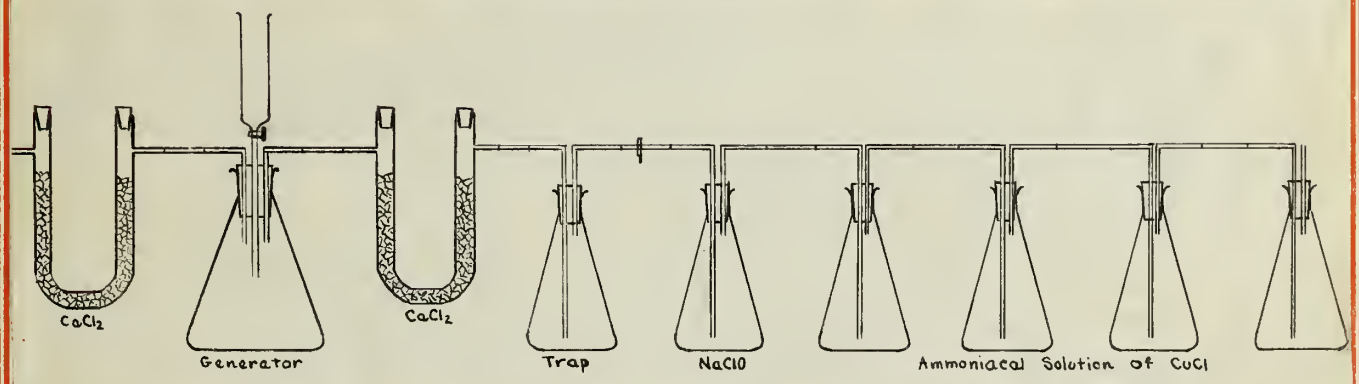
with a heavy charge of lime, and the lime is covered by a charge of scrap and pig iron. After two hours, the heat of the furnace has softened this charge so that it has sunk, and then the final charge of scrap and pig are added. In order that the slag may at all times be rich in lime, small amounts are added from time to time according to the impurities present. The limit of CaO to be added is 55%, since more than this amount will form a viscous infusible slag. Manganese, if present, also assists in the removal of sulphur by forming MnS. The sulphur in this case is slowly oxidized and the manganese returns to the boiling solution of metal.

By the Basic Bessemer process, the sulphur and phosphorus are removed during the afterblow period, which is carried on in a converter. The converter is supplied with the molten metal and is blasted for a certain length of time depending upon the amount of impurities present. Lime is added in amounts sufficient to oxidize all the impurities. Some sulphur is oxidized during the blow and the remainder passes into the slag in the form of CaS.

EXPERIMENTAL.

On account of the method of manufacture of calcium carbide it most usually, as previously stated, contains impurities. The first step in the experimental work is therefore to ascertain the purity of the carbide, since it is to be used throughout this problem.

An exact amount of carbide was weighed out and placed in a dry flask. As shown in the diagram, the flask was connected with a dropping funnel, two $CaCl_2$ U-tubes and a train of flasks. The dropping funnel was filled with a 20% brine solution.



The gas was liberated by allowing the brine to drop on the carbide very slowly, and when the reaction seemed to cease, the generator was heated in order to complete the reaction; a saturated brine solution was used because acetylene is insoluble in it, and soluble in water. The first U-tube served to remove the moisture from the air current, which swept the non-absorbed gases into the solutions. The second U-tube served to catch the entrained moisture in the acetylene. The trap was employed to regulate the passage of the gas in the train of flasks, of which the first contained sodium hypochlorite to remove the hydrogen sulfide and phosphide, and the following four flasks con-

tained an ammoniacal solution of cuprous chloride to absorb the acetylene, by forming copper acetylide. This last compound is explosive when dry; but it can easily be dissolved in hydrochloric acid, after completing the experiment. The hypochlorite flask was weighed separately, and the four cuprous chloride flasks were weighed together, before and after the gas was generated. The gases were determined by gain in weight of their respective absorbing solutions; from five such edeterminations the carbide was calculated to be 45% pure.

The iron sulphide to be used in this work was also analyzed for its purity, by titrating against a standard solution of $KMnO_4$. An average of four results showed the FeS to contain 61.8% iron, but since it should theoretically contain 63.55% iron, this compound is only 97.24% pure.

To determine the value of calcium carbide as a metallurgical reducing agent, I have centered all my work on its desulphurizing effect on iron sulphide, because this is the most common form of sulphur occuring in steel. To begin with, the following would be the most probable reaction that would take place by heating the two compounds at a high temperature, assuming that the reaction would go to completion:

$$3CaC_2 + 3FeS = 3CaS * Fe_3C + 5C.$$

Since equal moles of the carbide and sulphide are necessary for the reaction, as indicated by the equation, one-fourth the molecular weights of each (considering their purity) were weighed accurately and mixed thoroughly; 22.5625 grams FeS and 35.55 grams CaC_2. This mixture was placed in a fire clay crucible and heated in a small pot furnace for four hours at a constant temperature of 1000°C. The resulting mass, formed one large, rather brittle lump, but did not fuse enough to pour. It was pulverized to a fine powder in an iron mortar,

during which time, necessary precautions were exercised to prevent any loss of the fine material.

Half of this pulverized mass was divided into two equal portions, and analyzed for the presence of free calcium carbide. The same method and apparatus used for the determination of the purity of the carbide, described in the beginning of the experimental work, was employed here. I wish to say, that all the results on this and following pages, are the best checks selected from analyses of four fusions, all the fusions being made under the same conditions and treatments; of course the results were taken from only one of the four complete analyses, and is not a collection of results taken from parts of each complete analysis.

Determination of free Calcium Carbide.

1	2
10.0275 gm. sample used	10.0275 gm. sample used
.8151 gms. C_2H_2 liberated=	.8090 gms. C_2H_2 liberated=
2.007 gms. free CaC_2	1.99 gms. free CaC_2

since the sample used is only 1/4 the total sample, the total free CaC_2 is equal to:

8.028 gms.	7.960 gms.

average value = 7.994 gms.

Sixteen grams of pure carbide were used to make the fusion, and the analysis indicate that only 7.994 grams remained. The missing carbide may have been dissipated in several ways; in the formation of CaS, CO_2, CaO, or C. From the following investigation, we can conclude that some of the carbide was used in the formation of CaS. The assumed CaS was washed out of a five gram sample of the fusion with several portions of boiling water, and the remaining residue was carefully dried, and later analyzed for its sulphur contents

in the form of FeS. Since CaS is hydrolized by water, reacting in this manner,

$$CaS + 2H_2O = Ca(OH)_2 + H_2S$$

the above washings contained $Ca(OH)_2$ in place of CaS. During the hydrolysis, a distinct odor of H_2S was detected, which verifies the above reaction and the presence of CaS in the fusion. To verify the presence of $Ca(OH)_2$, the washings were treated with $Na_2C_2O_4$, and a white characteristic precipitate of CaC_2O_4 was formed. The detection of the H_2S odor during hydrolysis is more conclusive evidence of the existence of CaS, than is the oxalate precipitate, since the latter may have been formed from the $Ca(OH)_2$ produced by the decomposition of the carbide by the water, or from the CaO which exists as an impurity in the carbide in unknown quantities.

Determination of the FeS reduced.

Analysis of the above Five Gram Sample from which the CaS has been thoroughly removed:

The sulphur was oxidized to sulphuric acid by fusion with 30 grams of pure sodium peroxide in a nickel crucible. This fusion was thoroughly washed out into a beaker, filtered, and treated with $BaCl_2$, to precipitate the sulphur as $BaSO_4$:

1	2
6.5698 gms. $BaSO_4$	6.5253 gms. $BaSO_4$
Sulphur equivalent=.904 gms.	Sulphur equivalent= .897 gms.
FeS " =2.479 "	FeS " =2.461 "
FeS in total fusion consisting of 40.1102 grams;	
19.85 gms.	19.72 gms.

average value=19.785 gms. FeS present.

22.5625 gms.FeS, which is equivalent to 21.92 gms. pure FeS, were used in making the fusion; therefore
21.92-19.75=2.135 gms. or 9.74% of the FeS was reduced.

The above results indicate a very low efficiency of calcium carbide as a desulphurizing agent; thus the carbide has no practical

value for the purpose intended under the administered treatment.

Therefore this investigation was further carried on by heating the same quantities of carbide and sulphide (35.55 gms. and 22.5625 gms. respectively) in a fire clay crucible. The temperature was kept constant at 1200° for four hours by the use of a gas pot furnace. The product obtained was a fused mass, of what appeared to be only iron, being much less brittle than the product obtained by the 1000° heat, and also had less free calcium carbide distributed over the surface. This was treated and analyzed in the very same manner as the previous fusion, and the following are the results:

Determination of Free Carbide.

1	2
9.2436 gm. sample used	9.2436 gm. sample used
.3624 gms. C_2H_2 liberated=	.3685 gms. C_2H_2 liberated=
.8932 gms. free CaC_2	.9079 gms. free CaC_2

This being only one-fourth of the total sample, the total free carbide will then be:

3.5728 gms. 3.6316 gms.

average = 3.6022 gms. free carbide.

Determination of the FeS reduced.

1	2
5.5885 gms. $BaSO_4$	5.5598 gms. $BaSO_4$
Sulphur equivalent = .768 gms.	Sulphur equivalent = .764 gms.
FeS " = 2.107 gms.	FeS " = 2.095 gms.

FeS in total fusion consisting of 36.9744 gms.:

15.583 gms. FeS 15.499 gms. FeS

average value = 15.541 gms. FeS present.

22.5625 gms. FeS, which is equivalent to 21.92 gms. pure FeS, were used in making the fusion; therefore

21.92 - 15.541 = 6.379 gms. or 29.152% of the FeS reduced.

By comparing the last results with those obtained by the 1000° fusion, we can almost conclude that at higher temperatures the reducing effect of the carbide is increased. But there must be some definite temperature at which all the carbide will enter into the re-

action, and it is obvious that at this temperature, the total reducing power of the carbide will be consummated. With this point of view, another fusion was made employing the same quantities of carbide and sulphide as used in the two previous fusions. The temperature was kept at 1400° C for one and a half hours by means of an oil pot furnace. At this high heat it was necessary to use a graphite crucible, the inside of which was lined with a smooth layer of fire clay. A hard, black, glossy, slag and a mass of iron was produced. The silica contained in the crucible lining also took part in the reaction, by helping in the slag formation. This last statement suggests the thought, that the addition of silica would probably lower the reaction temperature and lessen the time of operation, but this thought is contradicted by the fact that the lower temperature fusions (1000° and 1200°) were carried out in fire clay, silica containing crucibles which were not even slightly attacked after four hours of continuous heating. These crucibles contain 71.81% silica, most of which would have readily taken part in the reaction if there were need for it, as it was with the 1400° fusion.

An analysis of the mass of iron was made, for the determination of free calcium carbide, but not a trace could be detected. Applying the same method used in the previous analyses, the quantity of unreduced FeS was determined.

1	2
5 gm. sample used	5 gm. sample used
7.1023 gms. $BaSO_4$	7.1893 gms. $BaSO_4$
Sulphur equivalent = .977 gms.	Sulphur equivalent = .979 gms.
FeS " = 2.679 gms.	FeS " = 2.682 gms.
FeS in total fusion consisting of 19.6385 gms.:	
10.51 gms.	10.54 gms.

average = 10.525 gms. FeS present.

22.5625 gms. FeS, which is equivalent to 21.92 gms. pure FeS, were used in making the fusion; therefore
21.92-10.525 = 11.395 gms., or 52% of the FeS was reduced.

SUMMARY.

Since at 1400° C, all the calcium carbide takes part in the reaction in one form or another, it is evident that at this temperature the carbide produces its greatest reducing effect on ferrous sulphide. Higher temperatures may shorten the time of operation, but I doubt whether higher temperatures would be employed commercially for this purpose, because high heats tend to decrease the life of any furnace considerably.

The presence of silica is necessary for the formation of a running slag, which is a very important factor in large scale work.

With an efficiency of 52%, as the results indicate, the use of calcium carbide as a reducing agent for iron sulphide is not profitable on account of the high cost of the carbide. If a much cheaper method for the manufacture of carbide is developed, this process of reducing iron sulphide could be advantageously used on a commercial basis.

The reducing efficiency of calcium carbide cannot be entirely judged by its effect on ferrous sulphide alone, since it may render a greater efficiency in reducing oxides, other sulphide ores, and sulphur in steel and pig iron. Two other men who are independently engaged in investigations similar to this, have found that calcium carbide reduces from 35 to 55% of sulfur in steel, and also, that the reaction of carbide with ferric oxide begins at 1250° C and is completed at 1500° C.

The efficiency of 52% as indicated by the experimental results, does not take into consideration any sulphur that may have been oxidized to sulphur dioxide. In this light, the 52% efficiency is too

high. In order to determine the efficiency correctly, the amount of sulphur present in the slag must be determined. In the lower temperature fusions (at 1000° and 1200°) in which the reduced sulphur is in the form of calcium sulphide, the sulphur may be determined by absorbing the hydrogen sulphide in lead acatate during the hydrolysis of the calcium sulphide; this reaction is explained under the analysis of the first fusion. If more time were available, I would have made the above quantitative determinations of sulphur.

This problem, therefore, still has a momentous field open for investigation, which I hope will be further continued by those whose interest may have been aroused by this article.

I regret that I have only had one half year (one semester) to spend on this tremendous task and that so little could be accomplished, but I feel that the time was well spent, if this article will only give an impetus towards the completion of this investigation.

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